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Microstructural and Strength Stability of CVD SiC Fibers in Argon Environment

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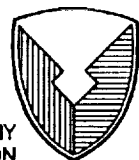U.S. Army Aviation Systems Command
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ABSTRACT

The room temperature tensile strength and microstructure of three types of commercially available chemically vapor deposited silicon carbide fibers were measured after 1, 10, and 100 hr heat-treatments under argon pressures of 0.1 to 310 MPa at temperatures to 2100^0C. Two types of fiber had carbon-rich surface coatings and the other contained no coating. All three fiber types showed strength degradation beyond 1400^0C. Time and temperature of exposure had greater influence on strength degradation than argon pressure. Recrystallization and growth of near-stoichiometric SiC grains appears to be the dominant mechanism for the strength degradation.

INTRODUCTION

Because of their high as-fabricated strength, modulus, chemical compatibility, and purity, chemically vapor deposited (CVD) SiC fibers are currently being used as reinforcement for silicon-based ceramic matrix composites. These composites are being developed for potential application in advanced heat engines where service temperatures may exceed 1400^0C. Previous studies[1] have shown that reinforced silicon nitride matrix composites fabricated by reaction forming methods show good room-temperature mechanical properties because at the fabrication temperatures near 1200^0C the CVD SiC fibers retain a great fraction of their as-fabricated strength. However, because of interconnected matrix porosity, these composites show poor oxidative stability at intermediate temperatures. This problem can be avoided by higher temperature fabrication approaches that yield fully dense matrices. But fully dense matrices fabricated by methods such as hot-pressing and hot-isostatic pressing show significantly lower ultimate tensile strength, primarily due to strength degradation of the fiber at the fabrication temperature and possibly due to reaction between the fiber and the matrix[2-3]. For optimizing the processing variables and for predicting long term durability of fully dense CVD SiC fiber reinforced composites, a basic understanding of thermo-mechanical stability of the fibers in fabrication environments and in contact with the matrix containing sintering additives are required.

This study had three major objectives: first, to determine the strength and microstructural stability of CVD SiC fibers in high temperature argon environments; second, to investigate the intrinsic strength degrading mechanisms; third, to suggest possible methods of improving their thermal stability.

EXPERIMENTAL

(1) Materials

Three types CVD SiC fibers produced by Textron Specialty Materials Division were studied. Manufacturer's designations for these fibers are SCS-0, SCS-6, and SCS-9. The fibers were produced by chemical vapor deposition of SiC onto a heated pyrolytic graphite coated carbon core with an outer diameter of 37 μm. Schematics of the fiber cross-sections are shown in Fig. 1(a). Both SCS-0 and SCS-6 fibers were grown to a diameter of ~ 140 μm and consist of two distinct zones. The inner zone consists of carbon-rich β-SiC grains and the outer zone of near-stoichoimetric β-SiC grains[4].

The SCS-9 was grown to a diameter of 75 μm and contained a single zone of near-stoichiometric SiC grains[5]. A complex carbon-rich coating[6] was also deposited on SCS-6 and SCS-9 fibers while SCS-0 fibers contained no surface coating. The approximate composition of this surface coating is shown in Fig. 1(b)

(2) Heat Treatments

The SiC fibers were heat-treated under argon pressures of 0.1, 138, and 310 MPa from 1200° to 2200°C at 200°C interval for 1, 10, and 100 hr. For all heat-treatments, batches of twenty-five individual fibers of length 125 mm were placed in grafoil envelopes and loaded in graphite furnaces. The type of furnaces used depended on argon pressure. For 0.1 MPa heat-treatment, a graphite lined induction furnace was used, whereas for high pressure argon treatments, a graphite resistance heated hot-isostatic press was used. Because graphite will oxidize more readily at lower temperature than SiC, it

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was assumed that the Grafoil envelops and the graphite lined furnaces significantly reduced any residual partial pressure of oxygen contained in the argon, thereby assuring intrinsic rather than oxidation effects on the fiber stability.

(3) Testing

Flexural strength measurements were performed by bending fibers around a cone-shaped brass mandrel. From base to apex, the cone diameter D decreased in discrete steps of $\delta(D)=0.76$ mm. Starting at the largest diameter step, each fiber was bent uniformly around the cone to a semi circle of length $0.5\pi D$. If fracture did not occur, the fiber was raised to the next smaller diameter step and the bending process repeated until fracture occurred. The flexural strength, σ_f, was calculated from the equation,

$$\sigma_f = Ed/D$$

where E is the fiber modulus, d is the fiber diameter, and D is the smallest cone at which the fiber fractured. For flexural strength measurements of SCS-0 and SCS-6 fibers, the values of E= 390 GPa[7] and d=0.142 mm, and for the SCS-9 fibers, the values of E= 331 GPa[5] and d=0.078 mm were used.

For room-temperature tensile testing, the fiber specimens were prepared by forming aluminum foil clamps at their ends, leaving 50 mm as gauge length. The aluminum foils were inserted in pneumatic grips, and the fiber specimens were pulled to failure using an Instron at a constant cross head speed of 1.3 mm/min. For each heat-treatment, tensile strengths of ten fibers were measured.

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(4) Microstructural Characterization

For microstructural analysis and grain size measurements, ~2 cm long fibers, both as-received and heat-treated, were embedded in an epoxy mold. The mold was initially ground on diamond impregnated metal discs and finally polished on a vibratory polisher using micro-cloth and 0.03 μm diamond slurry. The polished specimens were etched with Murakami's reagent or with flurocarbon plasma to delineate the grain boundaries, coated with a thin layer of palladium, and examined in a scanning electron microscope equipped with an energy dispersive X-Ray spectrometer (XEDS).

To determine phase stability, heat-treated fibers were analyzed by X-Ray diffraction (XRD). The XRD runs were made at a scanning speed of 1 deg/min using standard equipment with a Ni filter and Cu K$_\alpha$ radiation.

RESULTS

Strength After Exposure

The room-temperature flexural and tensile strengths of SCS-0, SCS-6, and SCS-9 fibers heat-treated in 0.1 MPa argon for 1 hr at temperatures up to 2100^{0}C are shown in Figs. 2 and 3, respectively. For comparison purposes, included in the figures are the room temperature strengths of untreated fibers. Each data point represents an average of ten individual tests and the error bars cover two standard deviations. For SCS-6 fibers, the as-fabricated flexural and tensile strength values of 6.0 and 4.0 GPa respectively, were maintained after heat-treatment to 1400^{0}C. Beyond this temperature, both strengths decreased continuously with increasing temperature up to 1800^{0}C and then reached plateaus. Although as-fabricated flexural

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and tensile strengths of SCS-0 and SCS-9 were significantly lower than those of SCS-6 fibers, both fibers showed strength loss trends similar to that of SCS-6 fibers.

The effects of one hour heat-treatment in the three argon pressures on the room temperature tensile strength of SCS-6 fibers are shown in Fig. 4. Results indicate that variation of argon pressure from 0.1 to 310 MPa had no significant effect on the strength degradation.

The room temperature tensile strength of SCS-6 fibers after 1, 10, and 100 hr heat-treatment in 0.1 MPa argon are shown in Fig. 5. It can be seen from Fig. 5 that at any temperature above 1200^0C, strength decreased with increasing time of exposure, but temperature had greater influence on strength degradation than time of exposure.

To determine the mechanisms of strength degradation of the CVD SiC fibers, x-ray, fractographic, and microstructural characterization were performed.

X-ray diffractometer traces of heat-treated fibers revealed sharpening of the diffraction peaks with increasing temperature of exposure; This is an indication of annealing of lattice strain or grain coarsening. Nonetheless, the crystal structure SiC remained cubic to 2000^0C. At 2200^0C, partial transformation of β to α SiC was noticed.

Since fibers usually broke into multiple pieces upon tensile testing, we were unable to unequivocally identify the primary fracture surface or the critical flaw responsible for the fracture of most of as-fabricated and heat-treated fibers. However, fractographic analysis

of some of the retained primary fracture surfaces indicates that the as-fabricated SCS-6 and SCS-9 fibers failed from a flaw at the core/ sheath boundary, and those fibers heat-treated beyond 1500^0C failed from a flaw closer to the outer surface of the SiC sheath (Fig. 6). For SCS-6 fibers, the nature of the flaw could not be determined even at high magnification. On the other hand, as-fabricated and heat-treated SCS-0 fibers fractured primarily from surface related flaws.

Figure 7 shows the evolution of microstructure with temperature for SCS-6 fiber heat-treated in 0.1 MPa argon for 1 hr. Also included in the figure for comparison purposes is the microstructure of as-fabricated fibers. As discussed previously, these fiber cross sections displayed four distinct regions; the innermost carbon-core region, followed by two distinct regions of SiC, and the outermost region of carbon-rich coating. Figure 7 shows that at 1400^0 and at 1600^0C slight coarsening of SiC grains contained in the outer zone was observed. At higher magnification, a distinct coarsening layer was noticed at the periphery of the outer zone of the fibers heat-treated at 1600^0C. At 1800^0C and beyond, exaggerated grains emanated from this coarsening layer region and grew towards the core. At 2000^0C, nearly 90% of the outer zone was covered with exaggerated grains. In contrast, the inner zone which contained carbon-rich SiC grains appeared to resist grain growth even with heat-treatment temperatures to 2100^0C.

SEM examination of the cross-sections of SCS-6 fiber heat-treated beyond 1800^0C showed segregation of particles to the unrecrystallized zone boundary as well as to the large SiC grain boundaries (Fig. 8).

Although the composition of these particles are still under investigation, XEDS analysis shows that these particles are complex silicides of Fe, Cr, Ni, and Ti.

Microstructural analysis of the cross sections of heat treated SCS-0 and SCS-9 fibers also showed reaction zone, grain growth, and segregation of metallic impurities in the outerzone SiC grains similar to that of SCS-6 fibers (Fig. 9).

The grain growth behaviors of outer zone SiC grains are shown in Fig. 10 for the three types of fibers heat-treated in 0.1 MPa argon from 1600^0 to 2100^0C for 1 hr. As the temperature of exposure increased the reaction zone in the outer zone also increased. The three fibers also displayed slightly different grain growth behaviors. The SCS-0 fiber showed greater tendency for grain growth compared to other fibers.

The kinetics of grain growth are shown in Fig. 11 for SCS-6 fibers heat treated in 0.1 MPa argon at 1500^0, 1600^0, and 1700^0C. Initially SiC grains grew rapidly and then the growth rate leveled off. Generally, the grain growth rate increased with increasing temperature.

A plot of the variation of the coarsening zone thickness with temperature is shown in Fig. 12 for SCS-6 fibers treated in 0.1 MPa argon for 1 hr. The dotted line in the figure represents the room-temperature tensile strength variation of SCS-6 fibers as shown previously in Fig. 3. It obvious from Fig. 12 that growth of reaction zone correlates well with the loss of tensile strength.

DISCUSSION

The three types of CVD SiC fibers investigated showed strength degradation above 1400^0C. The fact that strength degradation is independent of argon pressure or the type of fiber used, coated or uncoated, suggests that the degradation is intrinsic in nature. Fractographic analysis performed indicates the degradation is surface related. Supporting microstructural analysis reveals nucleation and grain growth in the outer zone of SiC sheath in the temperature range in which strength degradation was noticed. Based on these data it appears that the upper temperature limit of these CVD SiC fibers is controlled by the microstructural stability of near-stiochiometric SiC grains.

In general, the nucleation, recrystallization, and grain growth phenomena in ceramics are quite complex, and depend on temperature, grain size, growth or deformation related residual stresses, trace impurity level, and grain boundary mobility. Although the mechanisms of recrystallization and grain growth in CVD SiC fibers are still under investigation, one can offer a preliminary explanation for grain growth based on fiber microstructure and thermodynamic reasoning.

The CVD SiC fibers were fabricated near 1200^0C and contain SiC grains of diameter ranging from 20 to 100 nm[4]. The three types of fibers also contain noticeable amounts of trace metallic impurities (1000 PPM) primarily confined to the outer zone SiC sheath. Heating the fibers above their fabrication temperature should relieve growth related stresses; indication of this effect is seen in the XRD data. In addition, because of their high grain boundary surface area, these

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grains should recrystallize and grow at elevated temperatures. The temperature and the rate at which grain growth occur is a function of composition of SiC and trace impurity level. It is possible that metallic impurities present might have triggered recrystallization and growth of near-stoichiometric grains.

Although grain growth was prevalent in the outer zone, the inner zone which contained carbon-rich silicon carbide seemed to resist grain growth even at temperatures to 2100^0C. This observation is consistent with the general grain growth behavior of monolithic SiC[8] where carbon is known to inhibit grain growth. Based on this observation, it may be possible to improve the thermal stability of CVD SiC fibers by changing the microstructure of the outer zone from near-stoichiometric grains to carbon-rich grains. Of course the penalties for achieving improved, thermally stable carbon-rich SiC fibers are possibly lower elastic modulus and reduced oxidation resistance.

SUMMARY OF RESULTS

The influence of temperature, time, and argon pressure on the room-temperature strength of commercially available Textron CVD SiC fibers has been determined. The important findings are as follows.

(a) The CVD SiC fibers show strength degradation beyond 1400^0C

(b) Recrystallization and grain growth of the outer zone SiC grains appears to be the probable mechanisms of strength degradation.

(c) Inner zone SiC grains with carbon-rich boundaries show greater resistance to recrystallization than outer grains.

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(d) X-ray data show that β-SiC composition is stable to ˜2000^{0}C.

(e) The CVD SiC fibers contain appreciable amounts of Fe, Cr, Ni, and Ti impurities which appear to be confined to the outer zone and may play a role in the recrystallization process.

CONCLUSIONS

Thermal stability of CVD fibers appears to be dependent on the recrystallization and grain growth of the outer zone. Grain growth appears to be related to diffusion of impurities and/or stoichiometry of the grain boundary phases. Slow grain growth in the inner zone with carbon-rich boundaries suggests that this microstructure the fiber can improve strength stability of CVD SiC fibers.

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SCS-0 ⎫
SCS-6 ⎬ (~ 140 μm)
        ⎭

SCS-9
(75 μm)

Cross-section

— Pyrolytic graphite
  coated carbon core ⌐

— Inner zone:
  carbon-rich β-SiC

— Outer zone:
  Stoichiometric β-SiC ⌐

— Carbon-rich surface
  coating (0-4 μm) ⌐

Composition
of the surface
region

SCS-0 fiber

$\frac{Si}{C}$

1.0

β-SiC

0

Distance from
the surface,
μm

SCS-6 fiber and SCS-9
(DC)

$\frac{Si}{C}$

1.0

β-SiC

0

1   3

Distance from
the surface,
μm
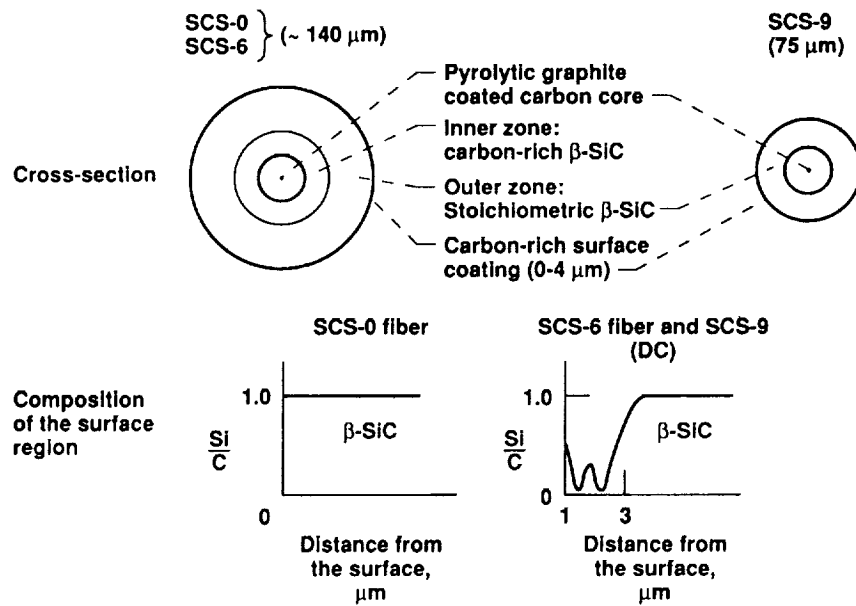
Figure 1.—Schematic showing CVD SiC fiber cross sections and surface coating
compositions.

Flexural strength, GPa

● SCS-6
▲ SCS-0
■ SCS-9

25 1000 1200 1400 1600 1800 2000 2200
Temperature, °C
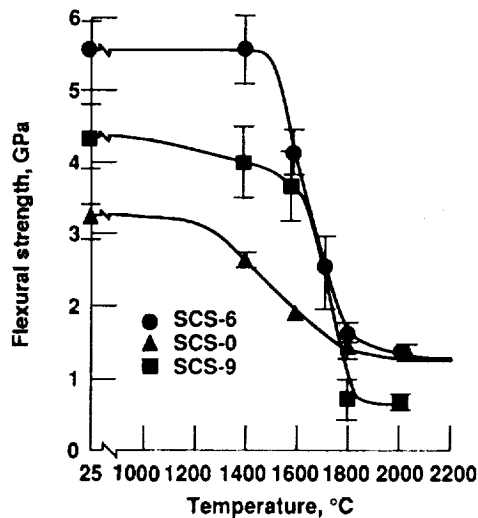
Figure 2.—Room-temperature flexural
strength of SCS-0, SCS-6, and SCS-9
fibers after 1 hr exposure in 0.1 MPa
argon pressure at elevated temperatures.

Gauge length = 50 mm

Tensile strength, GPa

● SCS-6
■ SCS-0
▲ SCS-9

25   1000 1200 1400 1600 1800 2000 2200
Temperature, °C
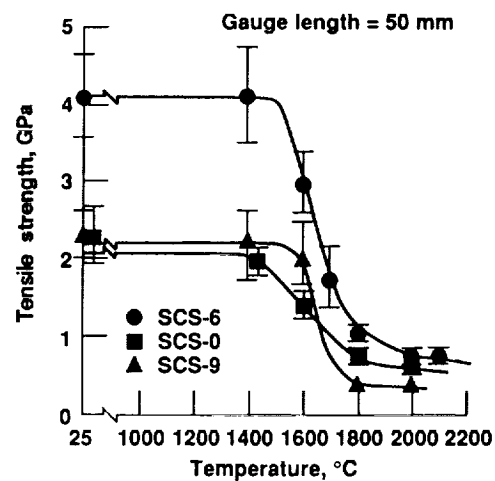
Figure 3.—Room-temperature tensile
strength of SCS-0, SCS-6, and SCS-9
fibers after 1 hr exposure in 0.1 MPa
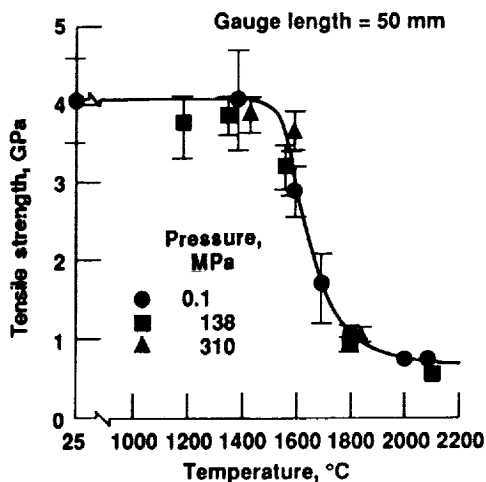argon pressure at elevated temperatures.

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Figure 4.—Effect of temperature and argon pressure on the room-temperature tensile strength of SCS-6 fibers heat-treated for 1 hr.
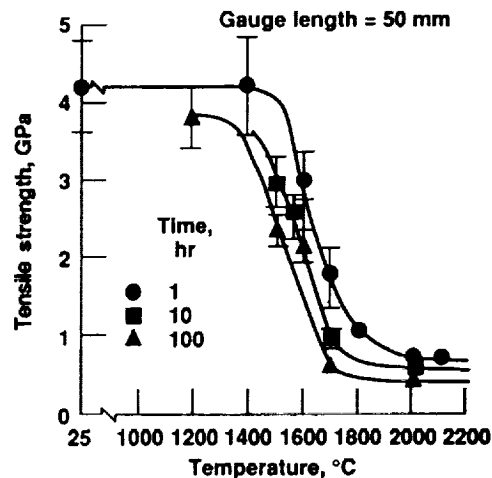

Figure 5.—Effects of temperature and time on the room-temperature tensile strength of SCS-6 fibers heat-treated for 1 hr in 0.1 MPa argon.

(a) As- fabricated.　　　　　　(b) Heat treated at 1700 °C for 1 hr.

Figure 6.—SEM photographs of SCS-6 fibers showing tensile fracture origin.

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(a) As-received. (b) 1400 °C. (c) 1600 °C.

(d) 1800 °C. (e) 2000 °C. (f) 2100 °C. 20 μm
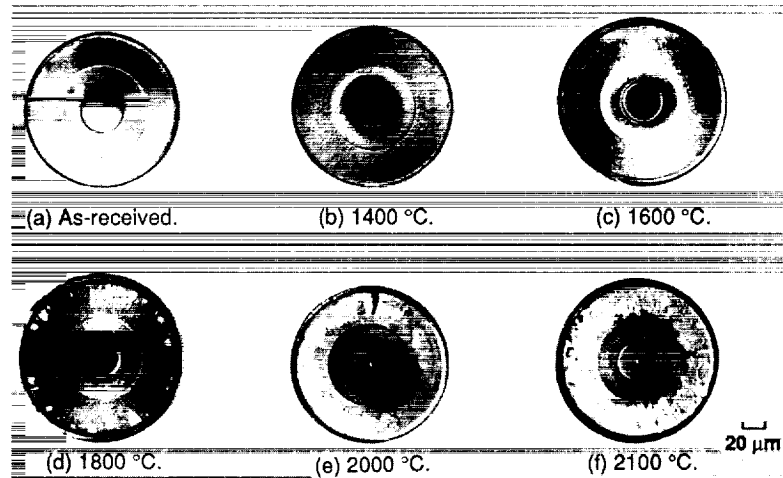
Figure 7.—Etched cross-sections of SCS-6 fibers before and after heat-treatment at elevated temperatures in 0.1 MPa argon for 1 hr showing grain growth.
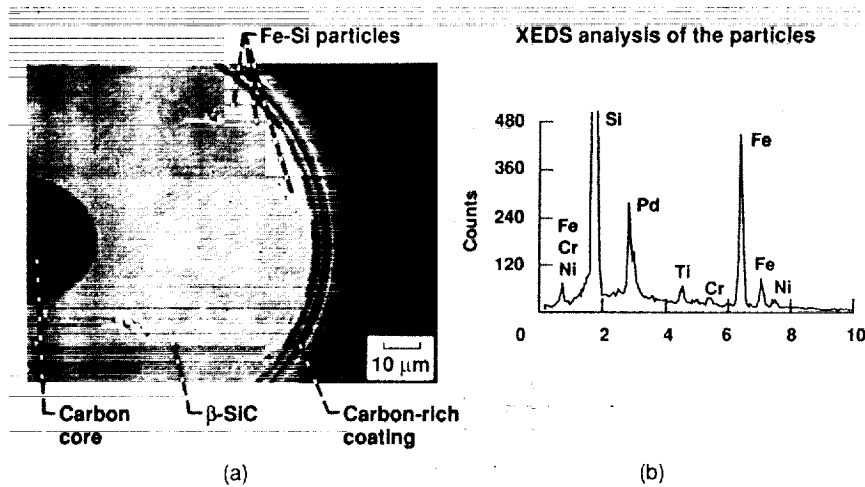

Fe-Si particles   XEDS analysis of the particles

Carbon core   β-SIC   Carbon-rich coating

(a)   (b)

Figure 8.— (a) SEM photograph of a cross-section of SCS-6 fiber heat-treated at 2000 °C showing particles in the outer zone. (b) XEDS analysis of the particles.

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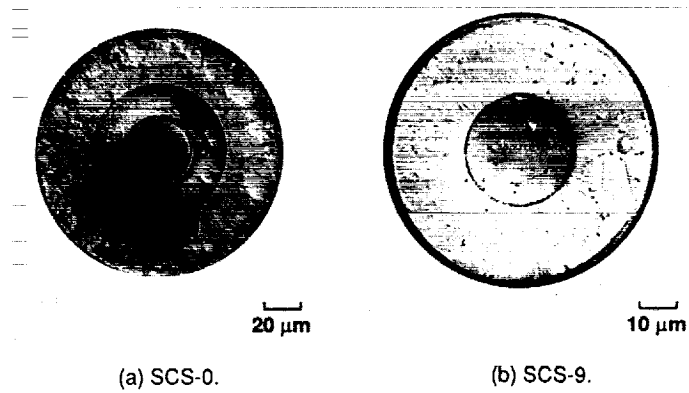20 μm   10 μm

(a) SCS-0.   (b) SCS-9.

Figure 9.—Etched cross-sections of SiC fibers heat-treatment in 0.1 MPa argon at 1800 °C for 1 hr showing grain growth.
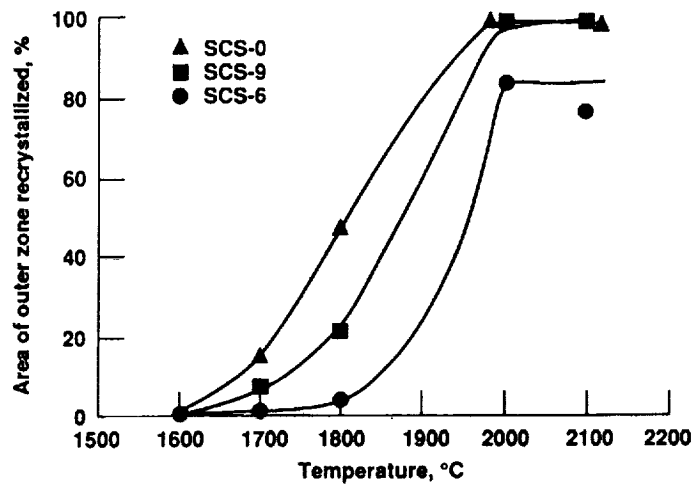

Figure 10.—Coarsening zone width as a function of temperature for CVD SiC fibers heat-treatment in 0.1 MPa argon for 1 hr.
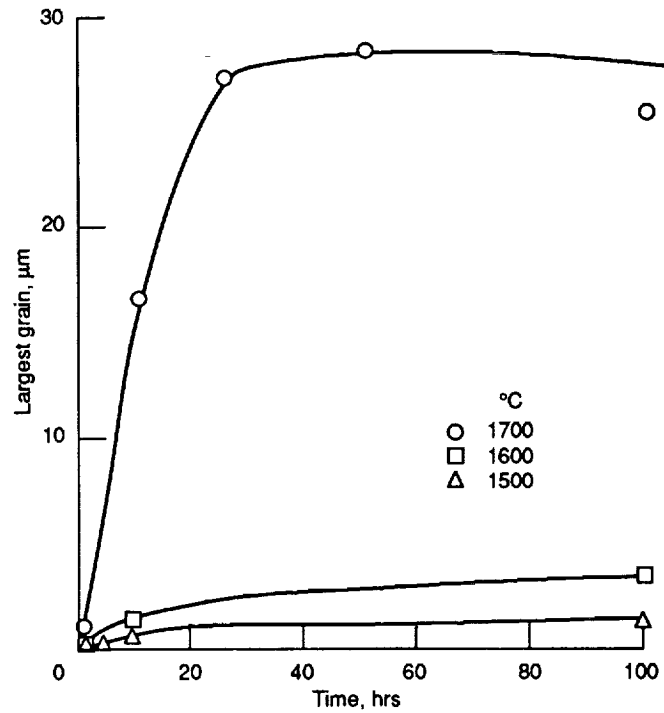
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Figure 11.—Growth behavior of near-stoichiometric SiC grains in SCS-6 fibers heat-treated from 1500° to 1700°C in 0.1 MPa argon.
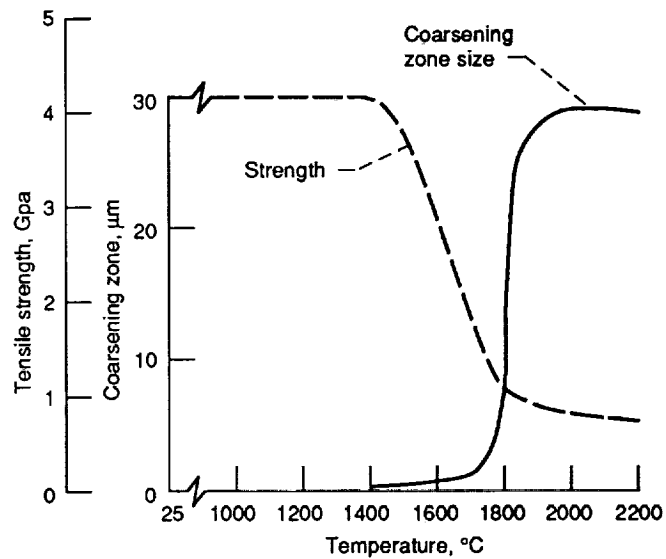

Figure 12.—Comparison of tensile strength and grain growth data for SCS-6 fiber heat treated in argon for 1 hr from 25 to 2100°C.

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16. Abstract

The room temperature tensile strength and microstructure of three types of commercially available chemically vapor deposited silicon carbide fibers were measured after 1, 10, and 100 hour heat-treatments under argon pressures of 0.1 to 310 MPa at temperatures to 2100°C. Two types of fiber had carbon-rich surface coatings and the other contained no coating. All three fiber types showed strength degradation beyond 1400°C. Time and temperature of exposure had greater influence on strength degradation than argon pressure. Recrystallization and growth of near-stoichiometric SiC grains appears to be the dominant mechanism for the strength degradation.

17. Key Words (Suggested by Author(s))

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